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RECENT RESULTS ON LITHIUM ION CONDUCTORS

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Abstract—Conductivity data for several new lithium ion conductors are presented. Li_3N has a very open structure with intersecting tunnels in 2 dimensions. High ionic conductivity has been found at relatively low temperatures. Data indicate that the conductivity can be improved by suitable doping, as well as stoichiometric control.

Solid solutions of Li_3SiO_4 and Li_3PO_4 have also been investigated. The unit cell of Li_3SiO_4 contains two SiO_4^{4-} tetrahedra linked by 8 Li ions, which are distributed over 18 possible sites. An improvement of the conductivity of about five orders of magnitude at 100°C has been obtained at 40 mole % Li_3PO_4 .

Solid LiAlCl_4 has relatively large values of conductivity in the range from room temperature to its melting point at about 146°C . Upon melting, the ionic conductivity jumps to over $0.1 \Omega^{-1} \text{cm}^{-1}$.

Another group of materials are based upon the anti-fluorite structure. Data are presented on Li_2S and Li_2O . The related compounds Li_5AlO_4 , Li_5GaO_4 , and Li_6ZnO_4 have a partially occupied cation sublattice. The ionic conductivity of these materials rises very rapidly at about 380°C , reaching very high values over 400°C .

The large values of ionic conductivity found in some of these materials may lead to their practical use as solid electrolytes.

INTRODUCTION

There has been rapidly accelerating interest in solid electrolytes in recent years, partly because of the interesting scientific problems which they pose, and partly because of their potential application in a number of important technological devices, as well as in a variety of experimental arrangements which can be utilized to acquire scientific information about phenomena or other materials. Major utilization to date has involved the employment of oxide ion conductors at elevated temperatures to measure and control oxygen partial pressures and activities, and sodium ion conductors (notably materials of the sodium beta alumina family) as solid electrolytes in elevated temperature battery systems. A variety of silver ion conductors are being used in several room temperature electrical devices, such as timers and coulometers, and a fluoride ion conductor is the active element in a commercially available selective ion electrode for use in analytical chemistry. There are, of course, many other possible applications for solid electrolytes if materials with proper characteristics can be found or developed. A number of these are listed in Table I.

Among the cationic conductors, a great deal of attention has been given to the beta alumina family in recent years, since it has been found that the ionic conductivity in those materials is extremely high at even moderate to low temperatures. Thus they can be of practical use in electrochemical systems involving elemental sodium as one of the electrodes. If one looks at battery systems, for example, it is obvious that those which involve the use of alkali metals at high activity provide the possibility of high specific energies.

While the beta alumina family represents a group of materials with very high conductivity for sodium

ions, there is no comparable known solid ionic conductor for either lithium or potassium at the present time. The highest conductivity values which have been reported to date for solid electrolytes which transport those ions also occur in the beta alumina family[1]. However, their conductivity values are several orders of magnitude lower than those found for sodium beta alumina[2].

Of special interest is the possibility of finding suitable solid electrolytes that can be used in lithium systems. Lithium has a lower equivalent weight than either sodium or potassium. It also is more electro-positive, and thus provides the possibility of greater cell voltages than the other two ions. Lithium has an additional advantage in that it can be much more easily handled at room temperature than the other alkali metals. Furthermore, several cathode materials are now known which might be employed in lithium-transporting systems because of their relatively high lithium diffusion coefficients. As well as being electronically conductive, they also provide relatively low values of lithium activity.

It is the purpose of the present paper to present some information on recent results on several groups of new lithium ion conductors. In several cases, the properties indicate that such materials might be interesting for practical purposes.

COMMENTS ON SOME OTHER LITHIUM ION CONDUCTORS

It has been known for some time that several materials exhibit very high values of lithium ion conductivity at elevated temperatures. Lithium tungstate, Li_2WO_4 , has high lithium ion conductivity in the range $684\text{--}738^\circ\text{C}$ in its alpha (cubic) phase[3]. Similarly, lithium sulfate, Li_2SO_4 [4], and various related

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Table 1. Examples of the application of solid state electrochemical techniques

Static emf measurements

Free energy of formation of binary and ternary compounds
 Free energy changes accompanying various cell reactions
 Thermodynamics of binary phases
 Determination of limits of stoichiometry of compounds
 Phase diagram determination
 Thermodynamics of phase transformations
 Effective mass of electrons or holes in semiconductors
 Solubility of gases in liquids

Time-dependent emf measurements

Phase boundary migration kinetics
 Supersaturation required for nucleation within and upon solids and liquids

Combinations of emf and current measurements

Diffusion in liquid and solid metals and mixed conductors
 Transport of both ionic and electronic species across phase boundaries
 Kinetics of condensation and vaporization processes
 Oxidation and reduction reactions on solid surfaces
 Thermodynamics of gaseous species
 Studies of the mechanism of catalysis
 Ionic and electronic partial conductivities in mixed conductors
 Structure of electrode-electrolyte interfaces

Technological applications

Batteries
 Fuel cells
 Catalysts
 Electrochromic display elements
 Variable resistors
 Thermoelectric devices
 Memory elements
 Solute valence control in semiconductors and ionic solids
 Purification of liquid and gases
 Measurement and control of liquid and gas compositions

materials[5-7] are also very good lithium ion conductors in certain elevated temperature phases. All of these materials, however, undergo phase transformations upon cooling and the lithium conductivity in the low temperature structures is greatly reduced.

Lithium iodide, which has the NaCl structure, has relatively high lithium ion conductivity at low temperatures[8]. There have also been reports that it can be doped with CaI[9], CaF_2 and CaO [8] which increase its conductivity. Likewise, a 2-phase mixture of lithium iodide and Al_2O_3 has been reported[10] to also have enhanced lithium conductivity.

There have been several investigations of lithium germanates[11], silicates[12-15], aluminosilicates[15-19], and a tantalate[20], which have indicated that some of them are moderately good lithium ion conductors. It is interesting to note that it has been found[17-19] that the lithium ion conductivity is greater in samples containing a noncrystalline phase, or in those containing both crystalline and noncrystalline regions, than in samples which are entirely crystalline.

Despite the broad range of this exploratory work, lithium beta alumina has continued to appear to be the best lithium ion conductor, although there are indications that lithium-containing beta alumina may not be thermodynamically stable[1]. It has also recently been reported[21] that the lithium ion con-

ductivity in this phase is enhanced if both lithium and sodium ions are present.

LITHIUM NITRIDE

Lithium nitride, Li_3N , has an unique structure consisting of hexagonal Li_2N layers connected by lithium ions which form N-Li-N bridges. It is thus very open, with large intersecting empty tunnels in two dimensions[22,23]. This structure is shown schematically in Fig. 1. While the crystal structure implies strong directional, and thus predominantly covalent, bonding, and the color ranges between ruby red and violet

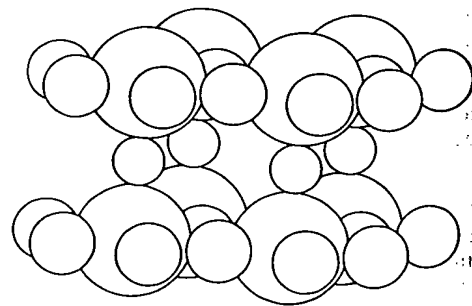


Fig. 1. Drawing of the Li_3N crystal structure. Small circles represent lithium atoms.

black[22, 24], there have been several different proposals concerning its electronic structure[25, 26].

Nuclear magnetic resonance experiments[27, 28] have indicated that the lithium ions are quite mobile in this structure. However, early ionic conductivity measurements on loose powders[29, 30] indicated relatively low values, in contradiction of the *nmr* results.

Some new measurements of the ionic conductivity of pressed and sintered pellets of Li_3N in our laboratory have recently been reported[31, 32]. Experiments were performed on two types of samples. One group was made from Li_3N purchased commercially (ROC/RIC Co.) which was claimed to be only 96% pure, the balance unknown. The other group were samples prepared in our laboratory by direct reaction of nitrogen with pure lithium ribbon (Foote Mineral, >99.9% purity). This reaction proceeds quite rapidly at low temperatures. The lithium was held at 170–180°C in a pure nitrogen atmosphere at 5–6 atm pressure for several hours, as suggested elsewhere[33, 34].

The reaction product was crushed to a fine powder and pressed at 2700 kg/cm² in a controlled atmosphere glove box. This was followed by sintering under purified nitrogen at 650°C. This procedure produced pellets with densities of about 80% of the theoretical value.

Conductivity measurements were made in a nitrogen atmosphere as a function of frequency between 20 and 550°C upon samples with ionically-blocking molybdenum electrodes. In order to assist the interpretation of the results, the frequency range was extended down to 0.01 Hz in some cases by using a PDP-8E digital computer for measurement and analysis. Use of the complex plane method of data

analysis allowed independent evaluation of the bulk ionic conductivity and interfacial effects[35].

The temperature dependence of the conductivity of these two sets of samples is shown in Fig. 2. It can be seen that these results are much higher than those reported earlier[29, 30], which are also included for comparison. It is interesting that the 96% pure material evidently has a higher conductivity than the purer samples. This indicates the influence of some unknown dopant.

Measurements were also made on the purer samples using solid lithium electrodes, which showed that there is essentially no interfacial polarization. The results of the very low frequency measurements also clearly indicated that the electronic conductivity is at least several orders of magnitude lower than the ionic conductivity in the temperature range investigated.

While the results on samples prepared by sintering in nitrogen and measured in the range 20–550°C did not show any dependence upon nitrogen pressure, samples annealed at about 750°C in 1 atm of nitrogen showed appreciably different behavior in two respects. There was a measurable, although small, amount of electronic conductivity.

Also, the ionic contribution to the conductivity was greatly increased, and exhibits a smaller temperature dependence at low to moderate temperatures than the samples that had not been subjected to this high temperature annealing treatment. These results are illustrated in Fig. 3.

These effects are probably associated with a variation in the Li/N ratio as a result of this treatment. We might assume that such samples are relatively more rich in lithium.

These ionic conductivity values are unusually high, being comparable to those obtained earlier[1] on

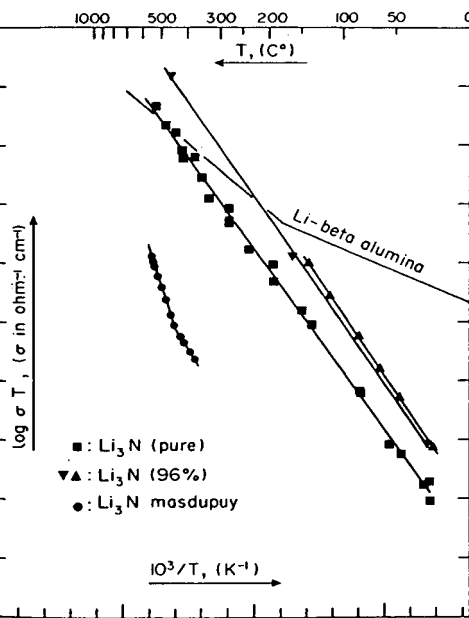


Fig. 2. Temperature dependence of the ionic conductivity of Li_3N . Circles indicate previous data[29, 30] obtained from loose powders. Single crystal conductivity of lithium beta alumina[1] is also shown for comparison.

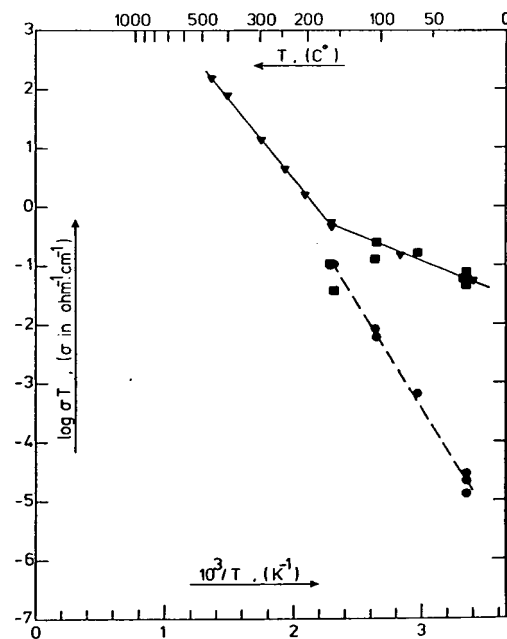
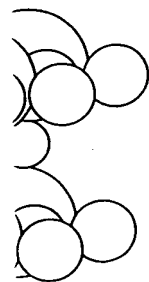


Fig. 3. Temperature dependence of the conductivity of Li_3N after 750°C anneal in 1 atm of nitrogen. Circles represent electronic conductivity.

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ique structure connected by lithium t is thus very open, els in two dimen- own schematically ure implies strong ly covalent, bond- uly red and violet



l structure. Smaller atoms.

Table 2. Conductivity data for lithium nitride

Material	Activation enthalpy (eV)	Temperature range (°C)	$\sigma_{25^\circ\text{C}}$	$\sigma_{100^\circ\text{C}}$	$\sigma_{200^\circ\text{C}}$	$\sigma_{400^\circ\text{C}}$	$\sigma_{450^\circ\text{C}}$
Li ₃ N (Pure)	0.61	25-520	3.7×10^{-8}	3.4×10^{-6}	1.5×10^{-4}	8.8×10^{-3}	1.7×10^{-1}
Li ₃ N (96%)	0.63	25-460	3.0×10^{-7}	3.8×10^{-5}	1.3×10^{-3}	8.6×10^{-2}	1.7×10^{-1}
Li ₃ N	0.19	25-180	2.0×10^{-4}	5.3×10^{-4}			
(Li-rich)	0.54	180-460			3.3×10^{-3}	1.2×10^{-1}	2.0×10^{-1}

single crystals of lithium beta alumina. Work is presently being undertaken to investigate both the effect of changes in stoichiometry and of doping in this material.

The relevant parameters relating to the conductivity data are included in Table 2.

SOLID SOLUTIONS BASED UPON LITHIUM ORTHOSILICATE

Previous work on a number of lithium silicates and aluminosilicates[15] has shown that the Li₄SiO₄ phase has the largest values of lithium ion conductivity in that group. Recently it has been shown[31, 36] that large enhancements in ionic conductivity can be obtained by forming appropriate solid solutions between Li₄SiO₄ and Li₃PO₄.

The structure of Li₄SiO₄ is made up of isolated tetrahedral SiO₄ anionic groups, with 8 lithium ions distributed over the 18 available cation sites in the stoichiometric composition[37]. The analogous orthogermanate, Li₄GeO₄, has a similar structure based upon tetrahedral anionic groups but the lithium ion distribution is differently ordered in the low temperature phase[37]. Ionic conductivity measurements on a group of lithium germanates have been reported recently[38].

Doping Li₄SiO₄ with Li₃PO₄ produces an extensive solid solution range in which the SiO₄ tetrahedra are replaced by PO₄ tetrahedra, and the difference in the anionic charge is compensated by a reduced concentration of lithium ions to be distributed among the available cation sites. Since the PO₄ tetrahedra also have a different size, the dimensions of the unit cell are also varied by doping, as indicated in Table 3. Extensive studies of the structure of these solid solutions have not been undertaken in our laboratory. We understand that this is being done elsewhere[39].

Polycrystalline samples of Li₃PO₄-Li₄SiO₄ solid solutions were prepared by standard ceramic procedures as already described[36]. Pellets were hot pressed at 1000°C and 350 kg/cm² for measurement

of the ionic conductivity. By this technique, polycrystalline samples 97-99% of theoretical density can be produced.

Conductivity values were derived from ac measurements upon these hot pressed pellets in air using the complex plane method of data analysis to provide a clear separation of bulk ionic conductivity and interfacial phenomena. Ionically blocking electrodes of both platinum and molybdenum were used. Reaction between lithium and platinum occurs above 400°C and thus limits the temperature range for the use of platinum electrodes. Measurements at higher temperatures using molybdenum electrodes required that they be protected against oxidation. This was accomplished by the deposition of a thin surface coating of platinum.

Direct current measurements were also made with lithium electrodes at temperatures up to 170°C in an evacuated system in order to verify that the charge transport is by the long range motion of lithium ions. No interfacial resistance effects were noted above 140°C in this case.

Table 3. X-ray lattice parameter data on Li₄SiO₄-Li₃PO₄ materials

Mole % Li ₃ PO ₄	a (Å)	b (Å)	c (Å)	β (degrees)
0	5.300	6.100	5.149	90.26
20	5.292	6.105	5.142	90.25
40	5.298	6.111	5.083	90.38
50	5.294	6.114	5.008	90.0
100	5.243	6.121	4.851	90.0

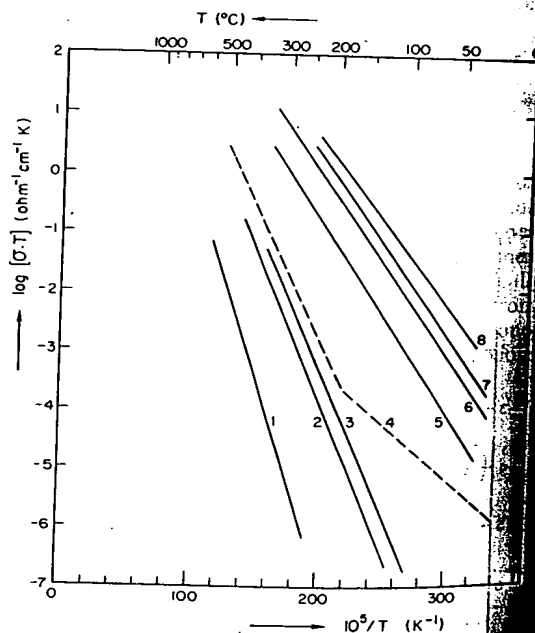


Fig. 4. Temperature dependence of the ionic conductivity of Li₄SiO₄-Li₃PO₄ samples. 1: Li₃PO₄; 2: 50 mole % Li₃PO₄; 3: Li₄SiO₄; 4: Li₄SiO₄, from West[13]; 5: 9.1 mole % Li₃PO₄; 6: 20 mole % Li₃PO₄; 7: 30 mole % Li₃PO₄; 8: 40 mole % Li₃PO₄.

Table 4. Conductivity data for $\text{Li}_4\text{SiO}_4\text{-Li}_3\text{PO}_4$ solid solutions

Mole %, Li_3PO_4	Activation enthalpy (eV)	Temperature range ($^{\circ}\text{C}$)	Conductivity at 100°C (Ωcm^{-1})
0.0	0.867	25-311	1.3×10^{-9}
9.1	0.659	25-346	2.0×10^{-6}
20	0.598	25-259	1.6×10^{-5}
30	0.598	25-196	3.2×10^{-5}
40	0.555	38-239	1.0×10^{-4}
45	0.620	25-285	2.2×10^{-6}
50	0.911	107-400	$3.2 \times 10^{-10*}$
100	1.305	154-614	$1.3 \times 10^{-11**}$

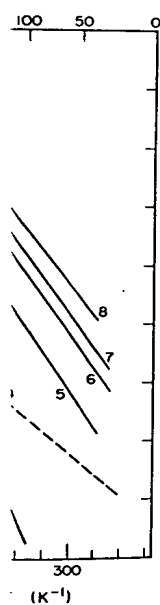
* Extrapolated data.

$\sigma_{450^{\circ}\text{C}}$
1.7×10^{-7}
1.7×10^{-1}
2.0×10^{-1}

unique, polycrystalline density can be

from measurements in air using the analysis to provide conductivity and ionizing electrodes of the used. Reaction is above 400°C , for the use of at higher temperatures required that this was accomplished by surface coating

also made with to 170°C in an that the charge of lithium ions. as noted above



ionic conductivity
: 2: 50 mole %
: West[13]; 5:
: 7: 30 mole %
: 4.

Ionically blocking electrodes (platinum) were also utilized with dc measurements to investigate the possibility of electronic conduction in these solid solutions. It was found that the electronic conductivity is at least six orders of magnitude lower than that due to the motion of ions.

The results of the ionic conductivity measurements on pure Li_4SiO_4 , pure Li_3PO_4 and various solid solution samples are shown in Fig. 4. Also included are some data presented earlier by West[13]. The apparent decrease in activation energy below about 180°C that he reported on the basis of monofrequency measurements was not found in our measurements. The results included in that figure show that Li_3PO_4 in solid solution can greatly enhance the ionic conductivity of Li_4SiO_4 . The magnitude of the enhancement is greater the lower the temperature, and amounts to some five orders of magnitude at 100°C . Parameters related to the conductivity of these solid solutions are presented in Table 4.

It is not presently known whether the large observed effects of the doping by Li_3PO_4 are primarily due to changes in the concentration and distribution of lithium ions among the available sites between the tetrahedral anionic groups or to the modification of the lattice through which the ions move.

ALKALI METAL CHLOROALUMINATES

Another group of materials whose structure can be viewed as consisting of cations lying between tetrahedral anionic groups is the alkali metal chloroaluminate family, with the general formula MAiCl_4 . In this case, the tetrahedral groups are the AlCl_4 anions.

These materials can be considered as ternary compounds between alkali metal chlorides and aluminum chloride in a 1:1 molar ratio. One of the unusual features of these systems is the presence of very low melting eutectics. In the Li, Na and K systems, the eutectic temperatures are 104°C [40], 107°C [41] and 128°C [42, 43], respectively, and they occur at compositions in the range 60-70 mole % AlCl_3 . These materials are interesting electrolytes in the molten state and have been investigated as molten salts by a number of authors[44]. They are also used as solvents in a number of liquid organic and inorganic solvents of interest as electrolytes at ambient temperatures. Here we will discuss recent measurements upon these ternary compounds between room temperature and their respective melting points[45, 46]. The melting points have been reported as 146°C [47],

153°C [41] and 256°C [47, 48] for the Li, Na and K compounds, respectively.

A thorough structural analysis has only been presented in the case of NaAlCl_4 [47, 49, 50]. The AlCl_4 tetrahedra are oriented with one face nearly parallel to the (001) plane. Alternate layers of tetrahedra point in opposite directions. Thus the chlorine ions can be viewed as forming pairs of layers perpendicular to the c-axis. The tetrahedrally coordinated aluminum ions, as well as the sodium ions, lie in the space between. The lattice of NaAlCl_4 is orthorhombic, whereas those of LiAlCl_4 and KAlCl_4 have been reported to be monoclinic, with β about 93° .

Solid samples of these ternary compounds were made by solidification directly from the liquid, which was prepared by melting together finely powdered mixtures of the alkali metal chlorides and aluminum chloride. The molten salts were purified carefully as described elsewhere[46] and solid samples were formed by pouring the molten salts into a Pyrex tube containing parallel molybdenum sheet electrodes held in place by Teflon spacers. Melting was done in a glove box containing a very pure and dry helium atmosphere.

Electrical conductivity measurements were carried out within the dry box using variable frequency ac

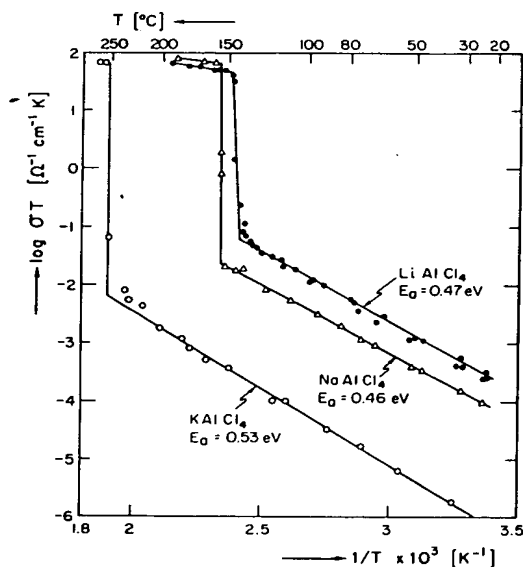


Fig. 5. Temperature dependence of the ionic conductivity of alkali chloroaluminates.

Table 5. Conductivity data for alkali metal chloroaluminates

Material	Activation enthalpy (eV)	Temperature range (°C)	Conductivity at 25°C (Ωcm^{-1})
LiAlCl ₄	0.47	25-146	1.2×10^{-6}
NaAlCl ₄	0.46	25-153	3.5×10^{-7}
KAlCl ₄	0.53	25-256	3.2×10^{-9}

techniques and the values of specific conductivity computed by interpretation of the complex impedance plane data.

The results of the conductivity measurements made on the compounds LiAlCl₄, NaAlCl₄ and KAlCl₄ in both the solid and liquid states are shown in Fig. 5. Data obtained upon both heating and cooling were in good agreement and there was no evidence of any time dependence. The curvature near the melting points may have been the result of some variation of the temperature within different parts of the sample. The relevant parameters related to these results are included in Table 5. It is seen that all three of these compounds have rather high values of ionic conductivity at ambient temperatures.

Direct current measurements were made using ionically blocking (molybdenum) electrodes and potentials between 20 and 400 mV. Analysis of these results indicated that the transference numbers of the electronic species are $<10^{-2}$, $<3 \times 10^{-3}$, and $<4 \times 10^{-2}$ for LiAlCl₄, NaAlCl₄ and KAlCl₄, respectively, at ambient temperatures.

Experiments are being undertaken to investigate the influence of doping upon materials of this family.

MATERIALS WITH THE ANTI-FLUORITE STRUCTURE

A number of oxides and fluorides which have the fluorite (CaF₂) structure have large values of anionic conductivity at elevated temperatures. Experiments have recently been undertaken to investigate the possibility of analogously high cationic conductivity in a group of alkali metal-containing materials which have the anti-fluorite structure.

It was previously shown[51] that Na₂S exhibits a moderately high sodium ion conductivity (1.7×10^{-4} (Ωcm^{-1}) at 400°C). This is increased by doping with 2 mole % NaCl to 8×10^{-4} (Ωcm^{-1}). In addition, encouraging results on LiF-doped Li₂O have been obtained at Hitachi[52]. The ternary phosphide Li_{8+4x}Sn_{1-x}P₄ has been studied by *nmr* techniques[53] which indicated that some of the lithium ions were rather mobile. Preliminary results on Li₃AlN₂ and Li₃BN₂ reported by Roth *et al*[54] also indicated appreciable ionic conductivity. All these materials crystallize in structures of the anti-fluorite type.

This section discusses recent results on Li₂S, Li₂O, and a group of materials (Li₅AlO₄, Li₅GaO₄, and Li₆ZnO₄) which have large concentrations of intrinsic cation vacancies in this structure[31, 55].

Samples of Li₂S were made by pressing and sintering powders of nominal 98% purity purchased commercially (ROC/RIC Co.). X-ray diffraction experiments on this material gave excellent agreement with

data in the literature[56, 57]. Sintering was conducted in the range 540-670°C in evacuated silica ampoules. In some cases, samples were doped with 10 mole % LiCl or 5 mole % ZnS to investigate the possibility of influencing the defect concentrations.

Conductivity measurements were made on pellets produced in this manner using lithium electrodes at temperatures up to the melting point of lithium. In order to make measurements at higher temperatures, ionically blocking molybdenum electrodes were also used. The measurements with lithium electrodes were made in a helium atmosphere, while those involving molybdenum were made in vacuum. Data are shown in Fig. 6.

When solid lithium electrodes were used, a time dependent conductivity was observed at temperatures below 60°C, with initially higher conductivity values decaying to steady state values about one order of magnitude lower. We assume that this is due to equilibration between the lithium electrodes and the Li₂S stoichiometry.

Measurements made using molybdenum electrodes under vacuum showed an increased value of activation enthalpy, as well as lower conductivity values, than in the case of samples measured with lithium electrodes. This difference is probably due to the fact that the chemical activity of lithium was not fixed

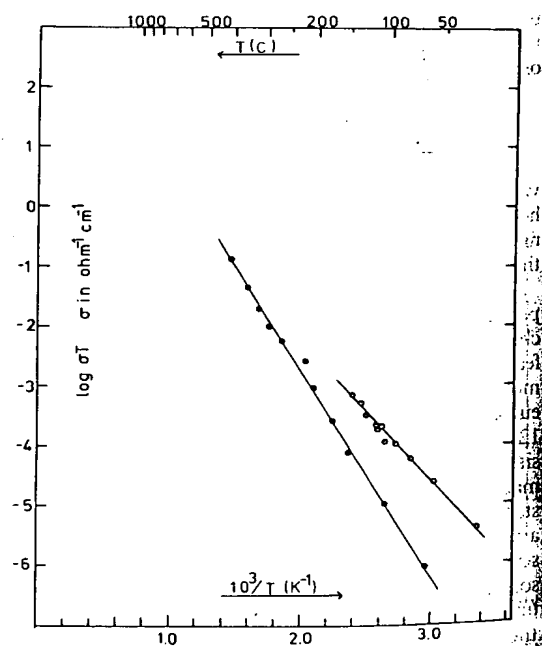


Fig. 6. Temperature dependence of the ionic conductivity of Li₂S. Upper curve obtained using lithium electrodes.

at unity in the experiments made with the molybdenum electrodes and so the lithium/sulfur ratio in the sample was not fixed, and was presumably different.

Measurements on the doped samples utilized lithium electrodes. Reproducible results were obtained in both cases, but the lithium ion conductivity was evidently not enhanced by the doping. It was also found in the case of the LiCl-doped samples that the conductivity apparently increases again at lower temperatures (below about 60°C). This may involve a temperature-dependent change in the defect equilibria between the lithium electrodes and the electrolyte at low temperatures.

Materials with the formulae Li_5AlO_4 , Li_5GaO_4 and Li_6ZnO_4 also have the anti-fluorite structure. However, if one considers the cation/anion ratio, which should be 2/1 for the ideal anti-fluorite structure, it is obvious that materials with these formulae have large concentrations of built-in vacancies in the cation sublattice: 25% vacancies in the first two cases, and 12.5% in the last.

These materials were synthesized by solid state reactions using either Li_2O or Li_2O_2 as the lithium oxide constituent. Pellets were prepared by both cold pressing and sintering in the range 600–750°C and by hot pressing at about 400–450°C in graphite dies. Above 400°C they all become mechanically soft and thus are readily deformed.

Since this structure consists of a face centered cubic arrangement of oxygen ions with the cations in tetrahedrally coordinated position between them, we can assume from the stoichiometry that vacancies exist upon the sublattice made up of these tetrahedrally coordinated sites. X-ray diffraction measurements showed that the materials which were prepared in this way had structures consistent with those presented in the literature[58–60].

Electrical conductivity measurements were made on polycrystalline pellets of these materials using variable frequency ac methods and ionically blocking electrodes (either silver or gold) in air.

All three materials were found to exhibit very similar conductivity behavior, as illustrated in Fig. 7. At low temperatures the conductivity obeyed the normal Arrhenius type of behavior, with activation enthalpies of 28.5, 20.6 and 17.5 kcal/mol for the aluminum, gallium and zinc-containing phases, respectively. At about 380°F the conductivity begins to increase rapidly over a range 60–80°C in all three cases, reaching very high values above about 450°C. At higher temperatures it also has a much lower temperature dependence. In the case of Li_5AlO_4 the conductivity is greater than $0.3 (\Omega\text{cm})^{-1}$ at 450°C. This value is comparable to those found in molten salts and is greater than the conductivity of either lithium beta alumina[1] or sodium beta alumina[2] at that temperature.

Direct current measurements were also made on a sample of Li_5AlO_4 using ionically blocking gold electrodes. They indicated a very small electronic contribution to the conductivity, so that we can assume that these materials transport charge by the motion of lithium ions.

Differential thermal analysis studies were also carried out and large endothermic peaks were found on

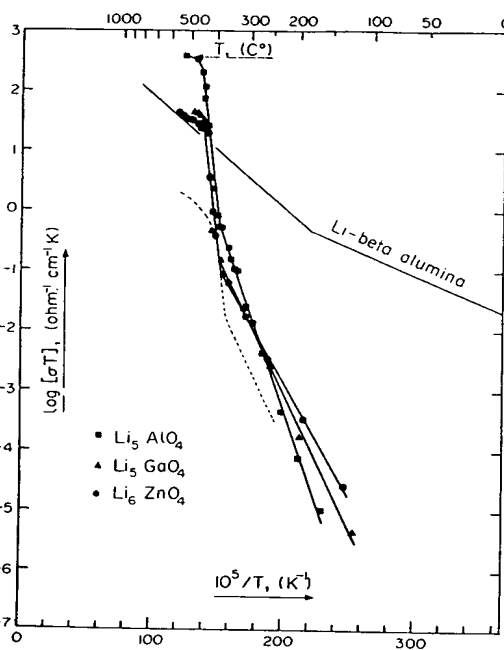


Fig. 7. Temperature dependence of the ionic conductivity of Li_5AlO_4 , Li_5GaO_4 , Li_6ZnO_4 , and Li_2O (dotted line). Single crystal lithium beta alumina data[1] also shown for comparison.

heating at about 385°C in all three materials. No crystallographic transformation has been reported at this temperature for any of these phases, but we can assume that these thermal effects relate to some type of change in the disorder within the cation sublattice.

Further experimental work is underway in our laboratory to attempt to understand this phenomenon and to investigate the influence of doping on materials of this type. It also appears that grain boundary and interfacial transport may be important in the high temperature regime.

Also included in Fig. 7 are the results of conductivity experiments on pure Li_2O . It can be seen that the shape of the temperature dependence in this case is very similar to that found for the ternary materials with large built-in defect concentrations. Li_2O is less attractive than the others for practical purposes, of course, because it is more readily attacked by H_2O and CO_2 .

Parameters related to the ionic conductivity of these materials are included in Table 6.

SUMMARY AND CONCLUSIONS

This paper has reported the results of exploratory work on several groups of new materials whose special characteristics may lead to their application as lithium-conducting solid electrolytes.

Lithium nitride has very high values of lithium ionic conductivity at moderate temperatures, and the conductivity is apparently strongly dependent upon both doping and stoichiometry. Preliminary work has indicated that values comparable to those of lithium beta alumina may be attained at ambient temperatures by proper annealing.

Table 6. Conductivity data for materials with the anti-fluorite structure

Material	Activation enthalpy (eV)	Temperature range (°C)	Conductivity ($\Omega \text{ cm}^{-1}$)			
			$\sigma_{100^\circ \text{C}}$	$\sigma_{200^\circ \text{C}}$	$\sigma_{400^\circ \text{C}}$	$\sigma_{450^\circ \text{C}}$
Li ₂ S (Li elect)	0.442	25-170	3×10^{-7}	—	—	—
(Mo elect)	0.737	50-410	2.5×10^{-8}	2×10^{-6}	1.8×10^{-4}	—
Li ₂ O	0.935	200-375	—	$\sim 2 \times 10^{-7}$	3.7×10^{-4}	—
Li ₃ AlO ₄	1.24	120-380	—	2.3×10^{-7}	3.2×10^{-3}	3.0×10^{-1}
Li ₃ GaO ₄	0.893	120-380	—	7.5×10^{-7}	5.8×10^{-4}	4.7×10^{-2}
Li ₆ ZnO ₄	0.759	120-380	—	1.2×10^{-6}	5.8×10^{-4}	3.2×10^{-2}

Materials with tetrahedral anionic groups appear to also have quite high values of lithium ionic conductivity and seem susceptible to major improvement by doping. Phosphate anion doping of Li₄SiO₄ appears especially useful, and increases the conductivity a number of orders of magnitude. In the case of LiAlCl₄, the temperature range of possible application in the solid state is limited by a rather low melting point. This may provide a hindrance to its use in certain solid state applications, but of course, provides the possibility of the use of this and related compositions as low temperature molten salt electrolytes.

The materials with the anti-fluorite structure and large concentrations of built-in cation vacancies show a very steep temperature dependence of the conductivity. At temperatures above 400°C their conductivities are unusually large, and as a result, they may be of interest for use as either solid electrolytes or separators in elevated temperature lithium battery systems. They may also be especially attractive for use in thermal batteries.

Several of these materials have the practical advantages of being stable in air, as well as being rather soft, so that they can be readily prepared at modest temperatures.

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